

TRANSITION METAL CARBIDES AND NITRIDES AS HYDROPROCESSING CATALYSTS

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INTRODUCTION

The removal of nitrogen and sulfur from petroleum and coal feedstocks is an essential step in their refining to transportation fuels. Traditional catalysts have been sulfides of Co, Mo, W and Ni in various combinations supported on alumina. Although other transition metal sulfides have been found to be more effective in hydrodesulfurization (Os, Ru, Ir, Rh), their high cost has precluded their use as commercial catalysts (1). The resemblance of early transition metal carbides and nitrides to Group 8 metals (2,3) suggested their possible application in hydroprocessing. The objective of this study was to compare the catalytic activity of selected carbides and nitrides to a commercial sulfided Ni-Mo-P/Al₂O₃ catalyst in the hydroprocessing of a diesel feedstock.

EXPERIMENTAL

The transition metal carbides and nitrides were prepared by a temperature-programmed method in which a precursor oxide was treated in a flowing reactive gas stream as the temperature was progressively raised (4,5,6). The catalysts were passivated in a stream of 0.5 mol% O₂/He after preparation. The surface areas of the catalysts were determined in a flow system by the 1-point BET method and were found to be 66 m²g⁻¹ for Mo₂C, 59 m²g⁻¹ for

Mo₂N, and 60 m²g⁻¹ for VN. Prior to catalytic evaluations the catalysts were reduced *in situ* at 723 K (450 °C) for 3h.

The performance of the carbides and nitrides was compared to that of a state-of-the-art commercial catalyst containing 14 wt% Mo, 3 wt% Ni, and 4-6 wt% P, supported on alumina. The surface area of the catalyst was 175 m²g⁻¹. This catalyst was sulfided in 10 mol% H₂S/H₂ at 623 K (350 °C) for 2 hours before the start of the reaction.

The catalysts were evaluated in a standard high pressure flow reactor system equipped with electronic flow and temperature controllers. The feedstock used for the evaluations was a finished diesel from a west coast refinery containing 0.02% S, 82 ppm N and 27 wt% aromatics. Hydrodenitrogenation was determined as N removed as ammonia as measured by the Antek N analysis of the product. Hydrodearomatization (HDA) was measured by the open column liquid chromatography (OCLC, ASTM D# 2549) method. The catalysts were compared at two conditions, moderate and severe, applied in succession to the same catalyst batch. The moderate conditions consisted of a LHSV of 3.0 h⁻¹, 4.8 MPa (700 psig), 573 K (300 °C) and a H₂ flow of 2000 SCFB. The severe conditions comprised a LHSV of 1.0 h⁻¹, 10.3 MPa (1500 psig), 653 K (380 °C), and a H₂ flow of 4000 SCFB. All catalysts were compared on an equal volume basis.

RESULTS AND DISCUSSION

The results of the catalytic evaluations are reported in Table 1 and 2. The tables also report the amounts of catalyst loaded in volume and weight. The comparisons are made at constant values of liquid hourly space velocity (LHSV), so that the hydrodenitrogenation activity (%HDN) of the different catalysts are on the basis of *equal volume*. For analysis, samples were collected at the reported time intervals, sometimes with mixing of aliquots.

Table 1 compares the performance of the catalysts at moderate conditions. The Mo₂C catalyst shows a decline in activity over the 64 h of test time. Such initial deactivation is normal in most hydroprocessing catalysts. In contrast, Mo₂N does not manifest any substantial deactivation and maintains its initial activity. The VN catalyst shows no catalytic activity at these conditions. The commercial Ni-Mo-P-S/Al₂O₃ catalyst shows the greatest HDN activity per unit volume.

Table 1
Catalytic Performance of Catalysts at Moderate Conditions
(Reactant N = 84 ppm, P = 4.8 MPa, T = 573 K, LHSV = 3.0 h⁻¹, H₂ flow = 2000 SCFB)

Catalyst	Volume cm ³	Weight g	Product N ppm	HDN %	HDA %	Comments
Mo ₂ C	4.3	5.2	68	17	-	24 h, cuts 1-3
			74	9.8	-	40 h, cuts 4,5
			77	6.1	-	64 h, cuts 6,7
Mo ₂ N	3.2	5.1	70	17	-	24 h, cuts 1,2
			71	16	-	48 h, cuts 3,4
VN	5.8	5.2	84	0	-	24 h, cuts 1-3
			84	0	-	40 h, cuts 4,5
			84	0	-	64 h, cuts 6,7
Ni-Mo-P	15	12.8	25	70	-	24 h, cuts 1,2

Table 2 reports the performance of the catalysts at severe hydroprocessing conditions. At these conditions all catalysts are active, including VN. Of the carbides and nitrides Mo₂N remains the most active, equalling the performance of the commercial Ni-Mo-P-S/Al₂O₃ in HDN and approaching it in hydrodearomatization. Interestingly, the carbide and nitride catalysts showed increased HDN activity with the progression of the test. This is contrary to what is generally found in hydroprocessing and suggests that the catalysts were not properly activated in the initial tests. This may explain the lower performance of these catalysts compared to the commercial Ni-Mo catalyst at the moderate conditions (Table 1).

It should be pointed out that comparisons of catalyst performance in HDN at the severe conditions employed in Table 2 may be misleading because of the high conversions achieved. This would tend to eliminate differences between catalysts. However, it should also be noted that in all comparisons a *volume* basis was employed. If correction is made for the surface areas of the catalysts, the carbides and nitrides would manifest higher activities.

Table 2
Catalytic Performance of Catalysts at Severe Conditions
(Reactant N = 84 ppm, P = 10.3 MPa, T = 653 K, LHSV = 1.0 h⁻¹, H₂ flow = 4000 SCFB)

Catalyst	Volume cm ³	Weight g	Product N ppm	HDN %	HDA %	Comments
Mo ₂ C	4.3	5.2	4	95	22	24 h, cut 8
			2	98	18	50 h, cut 9
Mo ₂ N	3.2	5.1	17	80	31	30 h, cut 5
			1	99	41	100h, cut 6
VN	5.8	5.2	27	68	6	24 h, cut 8
			14	83	11	50 h, cut 9
Ni-Mo-P	15	12.8	1	99	43	24 h, cut 3
			1	99	61	50 h, cut 4

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